Mixed bridged, dinuclear copper(II) complexes with dinucleating, pyrazole derived ligands

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Abstract

Mixed μ-OH or μ-halide, μ-pyrazolato dinuclear copper(II) complexes of 3,5-bis(pyridin-2-yl)pyrazole (HL), 3-(6-methylpyridin-2-yl)-5-(pyridin-2-yl)pyrazole (HL^1) and 3,5-bis(6-methylpyridin-2-yl)pyrazole (HL^2) have been synthesized and characterized. Their spectral and magnetic behaviour are also reported. The μ-OH compounds behave as a Curie–Weiss paramagnet, while the μ-halide complexes exhibit strong antiferromagnetic interactions.

Introduction

Research on the coordination chemistry of pyrazole-derived ligands has progressed very rapidly over the last few years. One of the major research areas of interest is on metallocycles of the type M(pz)$_n$M' where pz is the pyrazole or pyrazole-derived ligand [1]. Very recently, interest in these M(pz)$_n$M' compounds has increased due to the possibility of synthesis of mixed, μ-X, μ-pz bridged compounds. In particular, mixed μ-OH, μ-pz, Rh(III), Ni(II), Pd(II) or Pt(II) bridged complexes are very interesting due to the enhanced nucleophilicity of the OH group, evidenced by its high field proton nuclear magnetic resonance and its consequent reactivity [2, 3].

Recently we have reported [4, 5] a tetradentate, dinucleating pyrazole derived ligand: 3,5-bis(pyridin-2-yl)pyrazole (bpypz) affording strictly planar, dinuclear, di-μ-pz bridged complexes with first transition metal ions.

In this paper we are reporting μ-halide, μ-pz or μ-OH, μ-pz copper(II) mixed bridged complexes with bpypz (hereafter referred to as HL) and other very closely related molecules (Fig. 1). Their magnetic properties and reactivity are also reported.
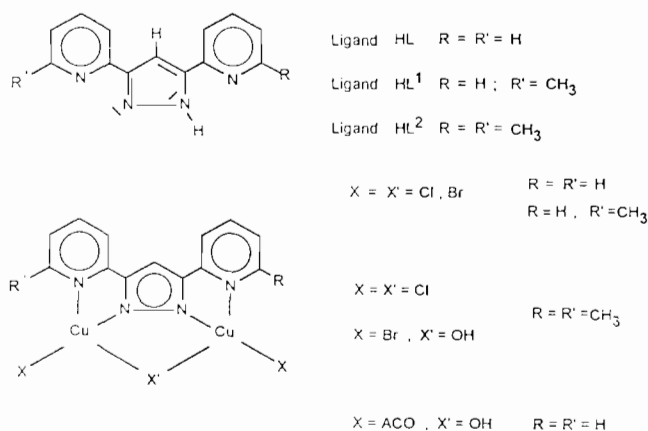

Fig. 1. Schematic drawing of the title compounds.

Experimental

General

All reagents were commercial grade materials and were used without further purification. All solvents were previously deoxygenated in a vacuum line and all reactions were routinely carried out under nitrogen atmosphere. The compounds 3,5-bis(pyridin-2-yl)-pyrazole (HL), 3-(6-methylpyridin-2-yl)-5-(pyridin-2-yl)-pyrazole (HL^1) and 3,5-bis(6-methylpyridin-2-yl)-pyrazole (HL^2) were synthesized as previously reported [4, 5].

Analyses (C, N, H) were performed in our micro-analytical laboratory on a Perkin-Elmer 240-B instrument. IR spectra were run on a Perkin-Elmer FT

spectrophotometer as KBr pellets or Nujol films. Electronic spectra were run on a Kontron V-UV spectrophotometer in solid state (KBr pellets, reflectance diffuse) or methanolic solution. Magnetic measurements were carried out on a Faraday type magnetometer (Manics DMS8) in the 300–5.8 K temperature range. The balance was calibrated with standard $Hg[Co(SCN)_4]$. Diamagnetic corrections were calculated from Pascal tables and direct measurements of the free ligand's magnetic susceptibility. Conductivity measurements were obtained with a radiometer model CDM-3 conductivity bridge in 10^{-3} M methanol solution.

X-ray powder diffraction data

The spectra were collected on a Siemens D-500 diffractometer with a Cu X-ray target operated at 20 mA and 40 KV using a graphite monochromator, scintillation counter and a conventional pulse height electronics. A wavelength $K\alpha_1 = 1.54059$ Å was used in all calculations. Data collection was performed under computer control (DEC PDP 11/34) using the commercial SIEMENS DIFFRAC-11/2 software package through a Daco-MP interface, which uses the VISSOR cell indexing program [6] and the APPLEMAN cell refinement program [7]. NaCl was added to the samples as d-spacing standard.

Synthesis of the copper halide complexes

To a solution of 0.1 g (L, 4.5×10^{-4} mol; L^1, 4.24×10^{-4} mol; L^2, 4.0×10^{-4} mol) of the corresponding ligands dissolved in 30 ml of deoxygenated ethanol, stoichiometric, solid $CuCl_2 \cdot H_2O$ or $CuBr_2 \cdot H_2O$ was added (Table 1). The solid which immediately appeared was kept in the mother liquor for 24 h with constant stirring, then was filtered under nitrogen atmosphere, washed with ethanol and dried under vacuum.

Synthesis of $[Cu_2L(CH_3COO)_2OH] \cdot H_2O$

To a solution of the HL ligand (0.1 g; 4.5×10^{-4} mol) in ethanol (20 ml), $Cu(CH_3COO)_2 \cdot 2H_2O$ (0.18 g; 9.0×10^{-4} mol) was added. The solution turned green–blue and then was concentrated almost to dryness. The green–blue crystalline solid which appeared, was filtered, washed with ethanol and ether and dried under vacuum.

Reactivity of the synthesized compounds with pyrazole

The reactivity of the synthesized complex compounds towards pyrazole was tested for all of them. No reaction was found in the case of the μ-halide complexes. The unaltered starting material was recovered in all cases. Only the μ-OH complexes react with pyrazole replacing the μ-OH group by a μ-pyrazolato group.

TABLE 1. Relevant data for the title compound

Compound	Yield (%)	Weight Cu salt (g)	N (%) Calc. Found	C (%) Calc. Found	H (%) Calc. Found	X (%) Calc. Found
Cu_2LCl_3	30	0.153	12.33 12.2	34.35 33.8	1.98 1.9	23.40 23.3
Cu_2LBr_3	32	0.201	9.53 9.4	26.55 26.3	1.54 1.5	40.78 40.4
$Cu_2L^1Cl_3$	61	0.145	11.95 11.8	35.86 35.6	2.35 2.3	22.73 22.1
$Cu_2L^1Br_3$	75	0.189	9.31 9.2	27.93 27.6	1.84 1.8	39.81 39.7
$Cu_2L^2Cl_3$	82	0.136	11.61 11.5	37.31 37.6	2.69 2.9	22.07 21.8
$Cu_2L^2Br_2(OH)$	89	0.179	10.15 10.0	32.56 32.7	2.53 2.5	28.89 28.7
$Cu_2L(Ac)_2(OH)$	72	0.182	11.59 11.7	42.24 42.1	3.34 3.3	
$Cu_2L^2Br_2(Pz)$	72		13.91 13.8	35.78 35.4	2.67 2.4	26.45 25.9

Synthesis of $Cu_2L^2Br_2(Pz)$

To a solution of pyrazole (0.012 g; 1.81×10^{-4} mol) in acetone (10 ml) a mixture of $Cu_2L^2Br_2(OH)$ (0.1 g; 1.81×10^{-4} mol) and acetone (20 ml) was added with constant stirring and heating (60 °C) for 30 min. The solid obtained was filtered, washed with acetone and methanol and dried under vacuum.

Results

General chemistry

By reaction of the corresponding halide copper salts with the pyrazole derivative ligands, the 2:1 copper(II) complexes (Cu_2LX_3) were synthesized. They have μ-halide bridges, except in the case of the HL^2 ligand and Br^- anion. This last complex presents a μ-OH bridge, probably due to the large ionic radius of the Br^- and the steric hindrance of the disubstituted pyrazole derivative ligand. This behaviour is similar to that found with the acetate copper(II) salt. The reaction of this salt containing the bulky anion acetate with the HL ligand gives only a μ-OH complex, not a μ-acetato derivative.

It is worth considering the different reactivity displayed by these compounds. μ-Halide complexes do not show any reactivity towards pyrazole or pyrazole derivative compounds, while μ-OH complexes easily react with pyrazole substituting the bridge –OH group by a bidentate pyrazole molecule, as was expected.

IR spectra

The IR spectrum of the copper–acetate complex shows the absorption bands assigned to the asymmetric and symmetric $\nu(CO)$ stretching modes at 1570 and 1441 cm^{-1}. The difference between the bands (129 cm^{-1}) is indicative of the unidentate coordination mode of the acetate anion [8]. All complexes display the typical absorption bands due to the pyrazole derivative ligands [4, 5]. No bands attributable to terminal or bridged halide ions could be seen.

Electronic spectra

Table 2 reports the electronic spectra of the synthesized complexes in methanol solution, compared with the spectra in solid state (KBr disk). Both spectra are reasonably similar in all cases, except for [Cu$_2$L(CH$_3$COO)$_2$OH]. Probably, the μ-OH bridge is quickly solvolysed in solution. No comparison could be made with the Cu$_2$L^{2}Br$_2$OH complex due to its insolubility in the more common solvents.

Conductivity measurements

Table 3 gives the conductivity measurements of the title complexes. The conductivity is larger in the more substituted ligands. However, the values obtained are sufficiently low to confirm the neutral, non-ionic character of these compounds. Probably, coordinate halide groups are present in these compounds, slowly substituted by solvent molecules in solution. Bromide ions are more easily solvolysed than chloride ions, as was expected. Typical values for 1:1 electrolytes in methanol solution are 80–115 Ω^{-1} cm^2 mol^{-1} [9].

Powder x-ray diffraction measurements

Compounds of the L ligand and those of the L^1 ligand behave identically. X-ray diffraction powder diagrams for both series are similar, showing small shifts in the observed lines. The most intense lines appear at $2\theta = 8.39$, 3.18 (L, X = Cl); 8.62, 3.22 (L, X = Br); $2\theta = 27.01$ (L^1, X = Cl); 26.71 (L^1, X = Br). All compounds in each series are isostructural, evidencing a similar molecular structure for the chloride and bromide copper(II) complexes for each ligand.

Ligand HL^2 behaves differently. No bromide complex could be isolated for this ligand, instead a μ-OH compound was synthesized. As was expected the μ-Cl and the μ-OH copper(II) complexes of the ligand HL^2 are not isostructural.

Magnetic susceptibility measurements

μ-Halide compounds behave differently from μ-OH complexes. μ-OH complexes exhibit a Curie–Weiss behaviour in the studied temperature range. No evidence of magnetic interactions between copper(II) atoms was found. From the Curie–Weiss plot the g value can be derived. For the [Cu$_2$L(CH$_3$COO)$_2$OH] and [Cu$_2$L^{2}Br$_2$OH] complexes, values of 2.3 and 2.2, respectively, were found.

For the μ-halide compounds the susceptibility data show a maximum near room temperature and a minimum at lower temperatures to increase again, probably due to paramagnetic impurities. This behaviour is characteristic of an overall antiferromagnetic interaction with a singlet ground state. Figure 2 shows the temperature-dependent molar magnetic susceptibility of a
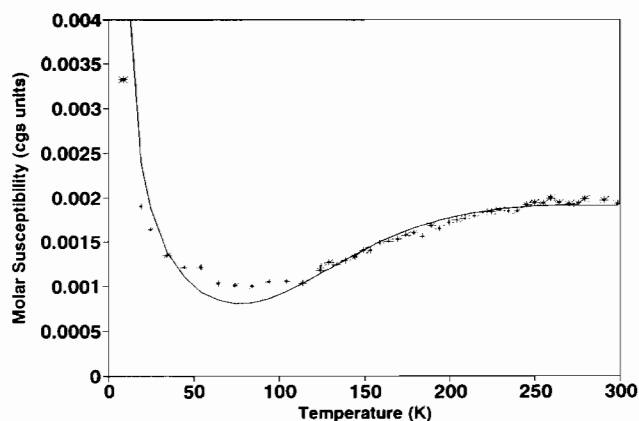
TABLE 2. Electronic spectra data

Compound	d–d band, λ (ϵ)	
	Methanol	Solid KBr
Cu$_2$LCl$_3$	717 (20)	710
Cu$_2$LBr$_3$	818 (30)	820
Cu$_2$L^{1}Cl$_3$	742 (59)	720
Cu$_2$L^{1}Br$_3$		
Cu$_2$L^{2}Cl$_3$	725 (31)	730
Cu$_2$L^{2}Br$_2$(OH)		
Cu$_2$L(Ac)$_2$(OH)	670 (10)	721

TABLE 3. Conductivity measurements

Compound	Λ_M (Ω^{-1} cm^2 mol^{-1})
Cu$_2$LCl$_3$	28
Cu$_2$LBr$_3$	34
Cu$_2$L^{1}Cl$_3$	44
Cu$_2$L^{1}Br$_3$	55
Cu$_2$L^{2}Cl$_3$	71
Cu$_2$L^{2}Br$_2$(OH)	75
Cu$_2$L(Ac)$_2$(OH)	68
Cu$_2$L^{2}Br$_2$pz	insoluble in methanol

Fig. 2. Plot of the molar magnetic susceptibility vs. temperature of a powdered sample of the Cu$_2$LCl$_3$ compound (*), with the calculated values (——) assuming a dimer model and parameters as given in Table 4.

TABLE 4. Fitting parameters assuming a magnetic dimer model

Compound	J	g	ρ	R
Cu_2LCl_3	-161.9	2.3	0.044	3.1E−09
Cu_2LBr_3	-170.6	2.3	0.020	1.4E−11
$Cu_2L^1Cl_3$	-180.2	2.1	0.000	5.6E−12
$Cu_2L^1Br_3$	-174.7	2.0	0.015	7.3E−12
$Cu_2L^2Cl_3$	-204.0	2.1	0.014	6.9E−10

powdered sample of the Cu_2LCl_3 compound as a typical example, with the calculated values (solid lines) assuming a dimer model and parameters as given in Table 4. All the other halide complexes exhibit a similar behaviour.

We interpret the magnetic behaviour of these compounds in terms of dinuclear formulation via a simple Bleaney–Bowers equation. The energy gap $2J$ between the singlet ground state and the triplet state is deduced from the magnetic data through the theoretical expression [10]

$$\chi_M = \frac{2Ng^2\beta^2}{kT}[3+\exp(-2J/kT)]^{-1}(1-\rho)$$
$$+\rho\frac{2Ng^2\beta^2S(S+1)}{3kT}+2N\alpha$$

where N, β, k and g have their usual meanings, ρ is the molar fraction of paramagnetic impurities and $N\alpha$ is the temperature independent paramagnetism (TIP) $(60.0\times10^{-6}$ cm^3 mol^{-1}/copper atom). The fitting was carried out using a non-linear minimizing procedure provided by the 'optimizer' facility of the Quattro Pro 4.0 spreadsheet (Borland international, Inc., 1992) allowing all the parameters, J, g and ρ to vary. The impurity is assumed to be Cu^{2+} ($S=1/2$), to have the same diamagnetic correction, molecular weight and g factor as the dinuclear complex, and to have a magnetic susceptibility that follows the Curie law [11]. The fit (R is the reduced chi square parameter of the fitting) is good enough as can be seen in Table 4 and Fig. 2, revealing strong antiferromagnetic interactions between copper(II) ions into the dimeric units.

Discussion

Recently we reported a structurally tetrameric copper(II) complex with the HL ligand in the solid state [12]: tetrakis{[(3,5-bis(pyridin-2-yl)pyrazolate)-(aqua)copper(II)]nitrate monohydrate}. This compound can be considered to be composed of two weakly associated pairs of dimers. Strong antiferromagnetic exchange intra-dimer interactions were found, attributed to the good overlap between the copper(II) and the ligand's magnetic orbitals in the strictly planar dinuclear moiety. It is well known that the Cu(II) ion in a square planar environment has its unpaired electron in a $d_{x^2-y^2}$ orbital [11], so any loss of planarity in the dimeric unit could negatively perturb the magnetic orbitals overlap.

Up to now, the crystal structure for the μ-halide or μ-OH compounds reported here has not been solved, but it is unlikely that the Cu(μ-OH)(μ-pz)Cu or Cu(μ-halide)(μ-pz)Cu core assumes a strictly planar geometry because of the large ionic radius of the OH and halide ions. Electronic spectra in solid state (KBr disk) are very similar to the electronic spectra in methanolic solution, except in the acetate, μ-OH complex (Table 2) and in all cases the absorption band position is indicative of a distorted tetrahedral coordination around the copper(II) ion [13, 14]. The coordination geometry is probably intermediate between tetrahedral and square planar. Further evidence for a distorted tetrahedral environment for the copper(II) ion in these compounds is provided by the magnetic measurements. A dimeric copper(II) anion, $Cu_2Cl_6^{2-}$, fully characterized by X-ray diffraction methods, has been reported in the literature. In this complex both copper(II) atoms exhibit a distorted tetrahedral coordination by chloride ions. Its magnetic behaviour displays strong antiferromagnetic interactions between both paramagnetic centres and its calculated g value ($g=2.20$) is in the range of that found in our complexes [15]. Consequently, it is quite reasonable to assume a similar coordination geometry for all of the mixed, μ-OH, μ-halide pyrazole derivative complexes reported in this paper.

The three chloride complexes exhibit a regular behaviour. Their J values are larger as the ligand becomes more substituted. The electron-donor effect of the methyl group could provide a simple explanation for this behaviour by increasing the electron density on the aromatic benzene ring and pyridinic nitrogen coordinating atom. The bromide complexes have comparable g values and exhibit similar antiferromagnetic exchange coupling as their corresponding chloride compounds. It remains intriguing to note the great difference observed in the magnetic behaviour of the μ-OH and the μ-halide compounds. Unfortunately, up to now we do not have any structural data to correlate these facts.

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